LOW-VISCOSITY ALLOPHANATES CONTAINING ACTINICALLY CURABLE GROUPS

Inventors: Christophe Détrembler, Liège (BE); Jan Weikard, Odenthal (DE); Dorota Gresza-Franz, Erkrath (DE); Frank Richter, Leverkusen (DE); Wolfgang Fischer, Meersbusch (DE); Jörg Schmitz, Köln (DE); Holger Mundstock, Wermelskirchen (DE)

Assignee: Bayer MaterialScience AG, Leverkusen (DE)

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Primary Examiner — Susan W Berman
Attorney, Agent, or Firm — Robert S. Klemez; Noland J. Cheung

ABSTRACT

A process for preparing binders containing allophanate groups which contain, at the oxygen atom of the allophane group that is bonded via two single bonds, organic radicals with activated groups capable of participating in a polymerization reaction with ethynyleically unsaturated compounds on exposure to actinic radiation; the process includes reacting A) one or more compounds containing urethane groups with B) one or more OH-functional compounds which contain groups capable of participating in a polymerization reaction with ethynyleically unsaturated compounds on exposure to actinic radiation, and C) optionally further NCO-reactive compounds, and D) in the presence of one or more compounds containing phenoxide groups, as catalysts. The binders can be used in preparing coatings, coating materials, coating compositions, adhesives, printing inks, casting resins, dental compounds, sizes, photoreists, stereolithography systems, resins for composite materials and sealants.

12 Claims, No Drawings
1. LOW-VISCOSITY ALLOPHANATES CONTAINING ACTINICALLY CURABLE GROUPS

CROSS REFERENCE TO RELATED PATENT APPLICATION

The present application is a divisional application of U.S. application Ser. No. 11/080,706, filed on Mar. 14, 2005 now U.S. Pat. No. 7,361,723.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to low-viscosity reaction products of polyisocyanates which contain activated groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, to a process for preparing them and to their use in coating compositions.

2. Description of the Prior Art

The curing of coating systems which carry activated double bonds by actinic radiation, such as UV light, IR radiation or electron beams, is known and is established in industry. It is one of the most rapid curing methods in coating technology.

Because of the environmental and economic requirements imposed on modern coating systems, that they should use as little organic solvents as possible, or none at all, for adjusting the viscosity, there is a desire to use coatings raw materials which are already of low viscosity. Known for this purpose for a long time have been polyisocyanates having an allophane structure as are described, inter alia, in EP-A 0 682 012.

In industry these substances are prepared by reacting a monohydric or polyhydric alcohol with excess aliphatic and/or cycloaliphatic diisocyanate (cf. GB-A 994 890, EP-A 0 000 194 or EP-A 0 712 840). This is followed by removal of unreacted diisocyanate by means of distillation under reduced pressure. According to DE-A 198 60 041 this procedure can also be carried out with OH-functional compounds having acid activated double bonds, such as hydroxalkyl acrylates, although difficulties occur in relation to the preparation of particularly low-monomer products. Since the distillation step has to take place at temperatures up to 135 °C, in order to be able to lower the residual isocyanate content sufficiently (<0.5% by weight of residue monomer), it is possible for double bonds to react, with polymerization, under thermal initiation, even during the purification process, meaning that ideal products are no longer obtained.

The preparation of low-monomer-content, allophane-containing, polyurethane-based, radiation-curing binders is described in EP-A 0 867 457 and U.S. Pat. No. 5,739,251. These binders, however, do not carry activated double bonds but instead carry reactive allyl ether groups (structure R—O—CH2—CH2—CH3). It is therefore necessary to add reactive ditens (low molecular weight esters of acrylic acid), which introduce the required UV reactivity.

EP-A 0 925 211 describes a process for synthesizing allophanate structures from oxazolidinones, although no radiation-curing derivatives having activated double bonds are known. All that is mentioned is the use of maleate- and/or fumarate-containing polyesters; the possibility of radiation curing is not described.

U.S. Pat. No. 5,777,024 describes the preparation of low-viscosity radiation-curing allophanates by reacting hydroxyfunctional monomers which carry activated double bonds with isocyanate groups of allophanate-modified isocyanurate polyisocyanates. The allophane-bound radicals are saturated as a result.

The formation of allophanate compounds by ring opening of urediones with alcohols is known in principle as a crosslinking mechanism in powder coating materials (cf. Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium 2001, 28th, 405-419, and also US-A 2003 0153 713). Nevertheless, the reaction temperatures required for this purpose are too high (≥120 °C) for a targeted preparation of radiation-curing monomers based on allophanate with activated double bonds.

Historically the direct reaction of uredione rings with alcohols to allophanates was first investigated for solventborne, isocyanate-free, 2K [2-component] polyurethane coating materials. Without catalysis this reaction is of no technical importance, owing to the low reaction rate (F. Schmitt, Angew. Makromol. Chem. (1989), 171, pp. 21-38). With appropriate catalysts, however, the crosslinking reaction between HDI-based uredione curatives and polyols is said to begin at 60-80 °C (K. B. Chandial; R. A. Englebach; S. L. Goldstein; R. W. Good; S. H. Harris; M. J. Morgan; P. J. Whitman; R. T. Wojcik, Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium, (2001), pp. 77-89). The structure of these catalysts has not been published to date. Commercial products prepared by utilizing this reaction are also undisclosed to date.

In summary it may be stated that the preparation of low-viscosity radiation-curing allophanates by ring-opening reaction of alcohols carrying activated double bonds with urediones at temperatures below 100 °C is not disclosed in detail in the prior art.

SUMMARY OF THE INVENTION

The present invention provides a process for preparing binders containing allophanate groups which contain, at the oxygen atom of the allophane group that is bonded via two single bonds, organic radicals with activated groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation; the process includes reacting

A) one or more compounds containing uredione groups with
B) one or more OH-functional compounds which contain groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation, and
C) optionally further NCO-reactive compounds, and
D) in the presence of one or more compounds containing phenoxide groups, as catalysts.

The present invention also provides a method of preparing coatings, coating materials, adhesives, printing inks, casting resins, dental compounds, sizes, photoreists, stereolithography systems, resins for composite materials and sealants. The method includes combining the above-described binders containing allophanate groups and one or more additives selected from the group consisting of UV absorbers, HALS stabilizers, pigments, dyes, fillers, levelling additives, devolatilizing additives, catalysts, and combinations thereof.

The present invention additionally provides coating compositions that include
a) one or more of the above-described binders containing allophanate groups,
b) optionally one or more polyisocyanates containing free or blocked isocyanate groups, which are free from
groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation,
c) optionally other compounds, different from those of a), which contain groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally contain free or blocked NCO groups,
d) optionally one or more isocyanate-reactive compounds containing active hydrogen,
e) initiators,
f) optionally solvents and
g) optionally auxiliaries and additives.

The present invention further provides substrates coated with coatings obtained from the above-described binders containing allophanate groups.

DETAILED DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc. used in the specification and claims are to be understood as modified in all instances by the term "about." It was an object of the present invention to provide a process for preparing binders containing allophanate groups and having activated double bond(s) which is accomplished with temperatures of below 100°C, the products thus obtainable preferably having viscosities at 23°C, in undiluted form, of \( \leq 100,000 \, \text{mPas} \).

Surprisingly it has now been found that from the reaction of uorethane with alcohols containing activated double bonds the desired binders can be obtained using phenoxy side salts as catalysts.

The invention accordingly provides a process for preparing binders containing allophanate groups which contain, at the oxygen atom of the allophanate group that is bonded via two single bonds, organic radicals with activated groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, where one or more compounds containing urethane groups is or are reacted with one or more OH-functional compounds which contain groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally further NCO-reactive compounds in the presence of one or more compounds containing phenoxazin groups, as catalysts, and optionally auxiliaries and additives.

Additionally the binders obtainable by the process of the invention are provided by the invention.

In component A) it is possible to use all organic compounds which contain at least one urethane group.

Preferably these are compounds obtainable by catalytic dimerization of aliphatic, cycloaliphatic and/or aromatic disocyanates or polycycosanates by methods which are known per se (cf. J. Prakt. Chem. 1994, 336, page 196-198).

Examples of suitable disocyanates include 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (HDI), trimethylhexane disocyanate, 1,3- and 1,4-diisocyanatodicyclohexylmethane, isophorone diisocyanate (IPDI), 4,4'-diisocyanatodicyclohexylmethanes, 1,3- and 1,4-diisocyanatobis(4-methylcyclohexane), and diphenylethane 4,4'-diisocyanate and diphenylmethane 2,4'-diisocyanate (MDI), 2,4- and 2,6-toluene diisocyanate (TDI), or mixtures thereof. 1,6-Diisocyanatohexane is preferred.

Examples of catalysts employed in this context include the following: trialkylphosphines, dimethylaminopyridines, tris (dimethylamino)phosphine.

The result of the dimerization reaction depends, in a manner known to the skilled person, on the catalyst used, on the process conditions and on the disocyanates employed. In particular it is possible for products to be formed which contain on average more than one urethane group per molecule, the number of urethane groups being subject to a distribution. Depending on the catalyst used, the process conditions and the diisocyanates employed, product mixtures are also formed which in addition to urethanes also contain other structural units, such as isocyanurate and/or iminooxadiazinedione, for example.

Particularly preferred compounds of component A) comprise products of the catalytic dimerization of HDI have a free HDI content of less than 5.0% by weight, an NCO content of 17-25% by weight, in particular of 21-24% by weight, and a viscosity at 23°C of from 20 to 500 mPas, preferably from 50 to 200 mPas.

The generally NCO-functional compounds obtainable by catalytic dimerization are preferably used directly as part of component A), but in principle they can also first be subjected to further reaction and only then used in A). This further reaction may be, for example, blocking of the free NCO groups or further reaction of NCO groups with NCO-reactive compounds having a functionality of 2 or more to form iminooxadiazinedione, isocyanurate, urethane, allophanate, biuret urea, oxadiazinetrione, oxazolidinone, acrylurea or carbodiimide structures. This gives compounds containing urethane groups and of higher molecular weight, which, depending on the chosen proportions, may contain NCO groups or may be free from NCO groups.

Blocking agents suitable for example are alcohols, lactams, oximes, malonates, alkyl acetocetates, triazoles, phenols, imidazoles, pyrazoles and amines, such as butanol oxime, disopropylamine, 1,2,4-triazole, dimethyl-1,2,4-triazole, imidazole, diethyl malonate, ethyl acetocetate, acetone oxime, 3,5-diisopropylpyrazole, e-caprolactum, N-tert-butylbenzylamine, cyclopentanone carboxylethyl ester or any desired mixtures of these blocking agents. The procedure for the blocking of NCO groups is well known to the skilled worker and described exemplarily in Progress in Organic Coatings 1999, 36, 148-172.

NCO-reactive compounds with a functionality of two or more can be the abovementioned di- and/or polycycosanates, and also simple alcohols with a functionality of two or more, such as ethylene glycol, propene-1,2-diol, propene-1,3-diol, diethylene glycol, dipropylene glycol, the isomeric butanediols, neopentyl glycol, hexane-1,6-diol, 2-ethylhexanediol and tripropylene glycol or else alkoxylated derivatives of these alcohols. Preferred dihydric alcohols are hexane-1,6-diol, dipropylene glycol and tripropylene glycol. Suitable trihydric alcohols are glycerol or trimethylolpropane or their alkoxylated derivatives. Tetrahydric alcohols are pentaerythritol or its alkoxylated derivatives.

The compounds of component A) can be used directly in the process of the invention or, starting from any precursor, can be prepared by prior reaction before the process of the invention is carried out.

By actinic radiation is meant electromagnetic, ionizing radiation, especially electron beams, UV radiation and also visible light (Roche Lexikon Medizin, 4th edition; Urban & Fischer Verlag, Munich 1999).

Groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation are for example vinyl, vinyl ether, propenyl, allyl, maleyl,
fumaryl, maleimide, dicyclopentadienyl, acrylamide, acrylic and methacrylic groups, preference being given to using activated groups of this kind such as vinyl ether, acrylate and/or methacrylate groups, more preferably acrylate groups, in the compounds of component B).

Examples of suitable hydroxyl-containing compounds of component B are 2-hydroxyethyl(meth)acrylate, poly(ethylene oxide mono(meth)acrylate (e.g. PEA6/PPE6; Laporte Performance Chemicals Ltd., UK), polypropylene oxide mono(meth)acrylate (e.g. PPA6, PPM25; Laporte Performance Chemicals Ltd., UK), poly(styrene oxide mono(meth)acrylate (e.g. PEM51, PEM63; Laporte Performance Chemicals Ltd., UK), poly(ε-caprolactone) mono(meth)acrylates (e.g. Tone M1005, Dow, Schwalmach, Del.), 2-hydroxypropyl(meth) acrylate, 4-hydroxybutyl(meth)acrylate, hydroxybutyl vinyl ether, 3-hydroxy-2,2-dimethylpropyl(meth)acrylate, the hydroxy-functional mono-, di- or higher molecular weight acrylates such as, for example, glyceryl di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate or dipentaerythritol penta(meth)acrylate, which are obtainable by reacting polyhydryl, optionally alkoxylated alcohols such as trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol.

Likewise suitable as a constituent of B) as well are alcohols obtained from the reaction of acids containing double bonds with epoxide compounds optionally containing double bonds, such as, for example, the reaction products of (meth)acrylic acid with glycidyl (meth)acrylate or bisphenol A diglycidyl ether.

Additionally it is likewise possible to use unsaturated alcohols which are obtained from the reaction of optionally unsaturated acid anhydrides with hydroxy compounds and epoxide compounds that optionally contain acrylate groups. By way of example these are the reaction products of maleic anhydride with 2-hydroxyethyl(meth)acrylate and glycidyl(meth)acrylate.

With particular preference the compounds of component B) correspond to the aforementioned kind and have an OH functionality of from 0.9 to 1.1.

Particular preference is given to compounds containing primary hydroxyl groups, since in the process of the invention they are more reactive than secondary or tertiary hydroxyl groups. Very particular preference is given to 2-hydroxyethyl acrylate and 4-hydroxybutyl acrylate.

Besides the OH-functional unsaturated compounds of component B it is possible in the process of the invention to use further compounds C) as well, which are different from those of B) and contain NCO-reactive groups such as OH, SH or NH, for example. These may be, for example, NH- or SH-functional compounds containing groups which react, with polymerization, with ethynyl unsaturated compounds on exposure to actinic radiation.

Additionally it is possible to incorporate groups having a hydrophilicizing action, particularly if use from an aqueous medium is envisaged, such as in an aqueous coating material, for example. Groups with a hydrophilicizing action are ionogenic groups, which may be either cationic or anionic in nature, and/or nonionic hydrophilic groups. Cationically, anionically or nonionically dispersing compounds are those which contain, for example, sulphonium, ammonium, phosphonium, carboxylate, sulphonate or phosphonate groups or the groups which can be converted into the aforementioned groups by forming salts (potentially ionic groups) or which contain polyelectrolyte groups and can be incorporated by means of existing isocyanate-reactive groups. Isoxazoline-reactive groups of preferred suitability are hydroxyl and amino groups.

Examples of suitable ionic compounds or compounds containing potentially ionic groups are mono- and dihydroxycarboxylic acids, mono- and diaminocarboxylic acids, mono- and dialdehydesulfonic acids, mono- and dioxinolsulphonie acids and also mono- and dioxynaphthalene acids and their salts, such as dimethoxypropion acid, dimethoxybutyric acid, oxypropionic acid, N-(2-aminoethyl)-β-alane, 2-(2-aminoethylamino)ethanesulphonic acid, ethylenediamine-propyl- or butylsulphonic acid, 1,2- or 3-propylenediamine-β-ethylenesulphonic acid, maleic acid, citric acid, glycolic acid, lactic acid, glycerine, alanine, taurine, lysine, 3,5-diaminobenzoic acid, an adduct of IPDI and acrylate (EP-A-0 916 647, Example 1) and its alkali metal and/or ammonium salts; the adduct of sodium bis(2-ethylhexyl) sulphate, the proploylated adduct of 2-butanol and NaHSO₄, described for example in DE-A 2 446 440 (page 5-9, formula I-111) and also structural units which can be converted into ionic groups, such as N-methylhydrazolamine, as hydrophilic synthesis components. Preferred ionic or potential ionic compounds are those possessing carboxyl or carboxylate and/or sulphonate groups and/or ammonium groups. Particularly preferred ionic compounds are those which contain carboxyl and/or sulphonate groups as ionic or potentially ionic groups, such as the salts of N-(2-aminoethyl)-β-alane, of 2-(2-aminoethylamino)ethanesulphonic acid or of the adduct of IPDI and acrylate (EP-A-0 916 647, Example 1) and also of dimethylopropanic acid. Suitable nonionically hydrophilicizing compounds are, for example, polyoxyalkylether ethers containing at least one hydroxyl or amine group. These polymers include a fraction of from 30% to 100% by weight of units derived from ethylene oxide. Suitable compounds include polymers of linear construction with a functionality of between 1 and 3, but also compounds of the general formula (I), in which

\[ R^1 \] and \[ R^2 \] independently of one another are each a divalent aliphatic, cycloaliphatic or aromatic radical having 1 to 18 carbon atoms, which may be interrupted by oxygen and/or nitrogen atoms, and

\[ R^3 \] is a polyalkylated polyethylene oxide radical.

Nonionically hydrophilicizing compounds are, for example, mono- or polyalkylenoxy ether polyether alcohols containing on average 5 to 70, preferably 7 to 55, ethylene oxide units per molecule, such as are obtainable in conventional manner by alkoxylating suitable starter molecules (e.g. in Ullmanns Encyclopädie der technischen Chemie, 4th edition, volume 19, Verlag Chemie, Weinheim pp. 31-38).

Examples of suitable starter molecules are saturated monoaethers such as methylol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, the isomers pentanol, hexanol, octanol and nonanols, n-decanol, n-dodecanol, n-tetradecanol, n-hexadecanol, n-octadecanol, cyclohexanol, the isomeric methylcyclohexanols or hydroxymethylcyclohexane, 3-ethyl-3-hydroxyethanol and/or ethoxyhydrofururyl alcohol, diethylene glycol monomethyl ethers such as, for example, diethylene glycol monomethyl ether, unsaturated alcohols such as allyl alcohol, 1,1-dimethylethanol alcohol or isopropyl alcohol, aromatic alcohols such as phenol, the isomeric cresols or methoxyphenols, arylalcoholic acids such as benzyl alcohol, anisyl alcohol or cinamyl alcohol, secondary monomers such as dimethyamine, diethyamine, dipropylamine, disopropylamine, dibutylamine, bis[2-ethylhexyl]amine, N-methyl- and N-ethylcyclohexylexylamine and diethyleneglycolmin and hydroxycarbonyl compounds, and also heterocy-
Cyclic secondary amines such as morpholine, pyrrolidine, piperaline or 1H-pyrazole. Particular preference is given to using diethylene glycol monobutyl ether as a starter molecule.

Alkyne oxides suitable for the alkylation reaction are, in particular, ethylene oxide and propylene oxide, which can be used in any order or in a mixture in the alkylation reaction.

The polyalkylene oxide polyether alcohols are either polyethylen oxide polyethers or mixed polyalkylene oxide polyethers at least 30 mol%, preferably at least 40 mol%, of whose alkylene oxide units are composed of ethylene oxide units. Preferred nonionic compounds are multifunctional mixed polyalkylene oxide polyethers which contain at least 40 mol% of ethylene oxide units and not more than 60 mol% of propylene oxide units.

Especially when using a hydrophilicizing agent containing ionic groups it is necessary to investigate its effect on the action of the catalyst D). For this reason preference is given to nonionic hydrophilicizing agents.

As compounds of catalyst component D) it is also possible, in addition to the phenoxides for use in accordance with the invention, to make use in principle of the compounds known per se to the skilled person for catalysing the reaction of isocyanate groups with isocyanate-reactive groups, individually or in any desired mixtures with one another.

Examples that may be mentioned here include tertiary amines such as triethylamine, pyridine, methylpyridine, benzyltrimethylenammonium, N,N-endethylepiperazine, N-Methylpyrrolidinone, pentamethyldiethylenetriamine, N,N-dimethylaminocyclohexane, N,N,N-dimethylaminoethanol, 1,4-diazabicyclo[2.2.2]octane (DABCO) or metal salts such as iron(II) chloride, tin(II) octoate, tin(II) ethylacrylate, tin(II) palmitate, dibutyltin(IV) dilaurate, dibutylin(IV) dicetate and molybdenum glycolate or any desired mixtures of such catalysts.

It is preferred, however, in D) to use exclusively phenoxides and/or compounds containing phenoxide groups as catalysts.

The compounds of component D) containing phenoxide groups preferably correspond to the general formula (II),

\[
\begin{align*}
    & \text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 \\
    & \text{X}_1 = \text{X}_2 = \text{X}_3 = \text{X}_4 = \text{X}_5
\end{align*}
\]

in which

Z is nitrogen or phosphorus,

R1, R2, R3, R4 independently of one another are hydrogen or identical or different optionally unsaturated, substituent-bearing or heteroatom-containing aliphatic, cycloaliphatic or aromatic radicals having up to 24 carbon atoms and Y is a phenoxide radical of the general formula (III),

\[
\begin{align*}
    & \text{Q} = \text{O} \\
    & \text{X}_1, \text{X}_2, \text{X}_3, \text{X}_4 \text{ independently of one another are substituents selected from the group consisting of hydrogen, halogen, cyano, hydroxyl, amide, amine, ether, ester, thioether, ketone, aldehyde and carboxylate group and also optionally unsaturated, substituent-bearing or heteroatom-containing aliphatic, cycloaliphatic or aromatic radicals having up to 24 carbon atoms, and optionally form parts of cyclic or polycyclic systems.}
\end{align*}
\]

As compounds of formula (I) containing phenoxide groups it is particularly preferred to use ammonium phenoxides and phosphonium phenoxides and especially preferred to use tetrabutylammonium phenoxides and tetraethylphosphonium phenoxides.

Phenoxides preferred in particular are tetrabutylammonium 4-(methoxy carbonyl)phenoxide, tetrabutylammonium 2-(methoxy carbonyl)phenoxide, tetrabutylammonium 4-formyl phenoxide, tetrabutylammonium 4-nitrophenoxide, tetrabutylphosphonium 4-(methoxy carbonyl)phenoxide, tetrabutylphosphonium 2-(methoxy carbonyl)phenoxide, tetrabutylphosphonium 4-formyl phenoxide, tetrabutylammonium 4-silyl carbonate and/or tetrabutylphosphonium silyl carbonate.

It is also possible to generate the aforementioned phenoxides of component D) in situ during the process. By using the corresponding phenols and strong bases such as tetrabutylammonium hydroxide or tetrabutylphosphonium hydroxide it is possible to generate the catalytically active phenoxides actually during the process.

It may be pointed out at this point that phenolic stabilizers of component E) may also react, by reaction with bases, to form phenoxides which function as catalysts for the purposes of component D). In that case it should be ensured that such phenoxides, in contrast to the corresponding phenols, no longer possess any stabilizing effect. It should also be borne in mind that strong bases such as tetrabutylammonium hydroxide or tetrabutylphosphonium hydroxide catalyse the formation of other isocyanate derivatives, especially the trimmerization.

It is also possible to apply the catalysts D) to support materials by methods known to the skilled person and to use them as heterogeneous catalysts.

The compounds of the catalyst component D) can be dissolved advantageously in one of the components participating in the process, or in a portion thereof. In particular the phenoxide salts for use in accordance with the invention dissolve very well in the polar hydroxyalkyl acrylates, so that D) in solution in small amounts of B) can be metered in as a concentrated solution in liquid form.

In the process of the invention the catalyst component D) is used typically in amounts of 0.001-5.0% by weight, preferably 0.01-2.0% by weight and more preferably 0.05-1.0% by weight, based on solids content of the process product.

As constituents of component E) it is possible in the process of the invention to make use, for example, of solvents or reactive diluents as well.

Suitable solvents are inert towards the functional groups present in the process product from the time of their addition up to the end of the process. Suitable solvents are, for example, those used in the paint industry, such as hydrocarbons, ketones and esters, e.g. toluene, xylene, isocyanate, acetone, butanone, methyl isobutyl ketone, ethyl acetate, butyl acetate, tetrahydrofurane, N-methylpyrrolidone, dimethylacetamide and dimethylformamide, though it is preferred not to add any solvent.

As reactive diluents it is possible to use compounds which in the course of UV curing are likewise (co)polymerized and hence incorporated into the polymer network and inert towards NCO groups. Such reactive diluents are described exemplarily, by way of example, in P. K. T. Oldring (Ed.), Chemistry & Technology of UV & EB Formulations For Coatings, Inks & Paints, Vol. 2, 1991, STA Technology.
London, pp. 237-285. They may be esters of acrylic acid or methacrylic acid, preferably of acrylic acid, with mono- or multifunctional alcohols. Examples of suitable alcohols include the isomeric butanols, pentanols, hexanols, heptanols, octanols, nonanols and decanols, and also cycloaliphatic alcohols such as isobornyl, cyclohexanol and alkylated cyclohexanols, bicycloheptanols, arylaliphatic alcohols such as phenoxethanol and nonylphenylethanol, and tetrahydropururfuryl alcohols. Additionally there is possible to use alkoxylated derivatives of these alcohols. Suitable dihydric alcohols include, for example, alcohols such as ethylene glycol, propane-1,2-diol, propane-1,3-diol, diethylene glycol, dipropylene glycol, the isomeric butanediols, neopentyl glycol, hexane-1,6-diol, 2-ethylhexanediol and tripropylene glycol or else alkoxylated derivatives of these alcohols. Preferred dihydric alcohols are hexane-1,6-diol, dipropylene glycol and tripropylene glycol. Suitable trihydric alcohols are glycerol or trimethylolpropane or their alkoxylated derivatives. Tetrahydric alcohols are pentaerythritol or its alkoxylated derivatives.

The binders of the invention must be stabilized against premature polymerization. Therefore, as a constituent of component E), before and/or during the reaction of components A) to D), preferably phenolic stabilizers are added which inhibit the polymerization. Use is made in this context of phenols such as para-methoxyphenol, 2,5-di-tertiary-butylhydroquinone or 2,6-di-tertiary-butyl-4-methylphenol. Also suitable are N-oxyl compounds for stabilization, such as 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO), for example, or its derivatives. The stabilizers can also be incorporated chemically into the binder; suitability in this context is possessed by compounds of the abovementioned classes, especially if they still carry further free aliphatic alcohol groups or primary or secondary amine groups and hence can be attached chemically to compounds of component A) by way of urethane or urea groups. Particularly suitable for this purpose are 2,2,6,6-tetramethyl-1-hydropiperidine N-oxide. Preference is given to phenolic stabilizers, especially para-methoxyphenol and/or 2,6-di-tertiary-butyl-4-methylphenol.

Other stabilizers, such as compounds from the class of the HALS (HALS=hindered amine light stabilizers), in contrast, are used less preferably in E), since they are known not to enable such effective stabilization and instead may lead to "creeping" free-radical polymerization of unsaturated groups.

In order to stabilize the reaction mixture, in particular the unsaturated groups, against premature polymerization it is possible to pass an oxygen-containing gas, preferably air, into and/or over the reaction mixture. It is preferred for the gas to have a very low moisture content, in order to prevent unwanted reaction in the presence of free isocyanate groups.

In general a stabilizer is added during the preparation of the binders of the invention, and at the end, in order to achieve a long-term stability, stabilization is repeated with a phenolic stabilizer, and optionally the reaction product is saturated with air.

In the process of the invention the stabilizer component is used typically in amounts of 0.001-5.0% by weight, preferably 0.01-2.0% by weight and more preferably 0.05-1.0% by weight, based on the solids content of the product.

The ratio of OH groups from component B) to the sum of NCO and uretdione groups from A) is typically from 1.5:1.0 to 1.0:1.9, preferably from 1.0:1.0 to 1.0:1.9, more preferably from 1.0:1.0 to 1.0:1.2.

The process of the invention is preferably carried out at temperatures of 20 to 100° C, more preferably of 40 to 100° C, in particular of 80 to 85° C.

Normally the NCO groups that may be present react more rapidly with the hydroxyl groups of component B) than do the uretdione groups of component A). It is therefore possible, if two or more different constituents are present in B), to control the uretdation and allopptionization by means of the sequence of addition of the constituents accordingly in such a way that one constituent of (B) is incorporated preferably with uretdation while the constituent added last is incorporated preferably with allopptionization.

It is, however, also possible to end the allopptionization by adding catalyst-deactivating compounds (in the case of the phenoxides, for example, strong acids such as acide phosphoric esters) or adding further isocyanate-containing compounds which scavenge the remaining compounds of components B) and C).

It is immaterial whether the process of the invention is carried out continuously in for example a static mixer, extruder or compounder or batchwise in for example a stirred reactor.

Preferably the process of the invention is carried out in a stirred reactor, the sequence of addition of components A)-E) being arbitrary.

The course of the reaction can be monitored by means of suitable measuring instruments installed in the reaction vessel and/or on the basis of analyses on samples taken. Suitable techniques are known to the skilled person. They include, for example, viscosity measurements, measurements of the refractive index, of the OH content, gas chromatography (GC), nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR) and near infrared spectroscopy (NIR). Preference is given to IR checking for any free NCO groups present (for aliphatic NCO groups, band at approximately ν=2272 cm⁻¹) and, in particular, for uretdione groups (e.g. band for uretdiones based on hexamethylene disiocyanate at ν=1761 cm⁻¹) and to GC analyses for unreacted compounds from B) and C).

In one preferred embodiment of the invention there is a parallel allopptionization and; uretdation of the compounds of component A). For that purpose A) is introduced initially, stabilizers and, where appropriate, further auxiliaries and additives from E) are added, subsequently components B)-E) are added and the reaction mixture is brought to reaction temperature.

In another preferred embodiment first of all A) is reacted with B) until the NCO groups have reacted completely, E) or parts thereof may already be present. Subsequently the reaction of the uretdione groups of A) with B) is initiated by adding D) and additionally, where appropriate, by adapting the temperature.

In one particularly preferred embodiment the isocyanate groups and the uretdione groups are reacted with an excess of hydroxyl groups of component B. The hydroxyl groups which remain following the reaction of A) with B), with catalysis of D), are subsequently reacted preferably with further isocyanate-containing compounds, in particular with those compounds described as possible constituents of component B), with uretdation.

The unsaturated allopphanes obtainable by the process of the invention, in particular those based on the products—employed preferably—if the catalytic dimerization of HDI, preferably have viscosities at 23°C of ≤100,000 mPas, more preferably ≤600,000 mPas, very preferably ≤40,000 mPas.

The unsaturated allopphanes obtainable by the process of the invention, especially those based on the products—employed preferably—if the catalytic dimerization of HDI,
preferably have number-average molecular weights $M_n$ of from 600 to 3000 g/mol, more preferably from 750 to 1500 g/mol.

The unsaturated aliphatic groups obtained by the process of the invention preferably contain less than 0.5% by weight of free di- and/or trisocyanate monomers, more preferably less than 0.1% by weight.

The binders of the invention can be used for producing coatings and paints and also adhesives, printing inks, casting resins, dental compounds, sizes, photoresists, stereolithography systems, resins for composite materials and sealants. In the case of adhesive bonding or sealing, however, a requirement is that, in the case of UV radiation, at least one of the two substrates to be bonded or sealed to one another is permeable to UV radiation; in other words, in general, it must be transparent. In the case of electron beams, sufficient permeability for electrons should be ensured. Preference is given to use in paints and coatings.

The invention further provides coating compositions comprising one or more binders obtainable in accordance with the invention, optionally one or more polyisocyanates containing free or blocked isocyanate groups, which are free from groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, optionally other compounds, different from those of a), which contain groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally contain free or blocked NCO groups, optionally one or more isocyanurate-reactive compounds containing active hydrogen, initiators, optionally solvents and optionally auxiliaries and additives.

The polyisocyanates of component b) are known per se to the skilled person. Preference is given here to using compounds optionally modified with isocyanurate, allophanate, biuret, uretdione and/or iminoxadiazinetriene groups and based on hexamethylene disiocyanate, isophorone diisocyanate, 4,4'-diisocyanatodicyclohexylmethane and/or trimethylhexamethylene disiocyanate.

The NCO groups in this case may also be blocked, blocking agents employed being the compounds already mentioned in connection with the description of component A).

The compounds of component c) include compounds such as, in particular, urethane acrylates based preferably on hexamethylene disiocyanate, isophorone diisocyanate, 4,4'-diisocyanatodicyclohexylmethane and/or trimethylhexamethylene disiocyanate, which optionally may have been modified with isocyanurate, allophanate, biuret, uretdione and/or iminoxadiazinetriene groups, and which contain no isocyanate-reactive groups containing active hydrogen.

NCO-containing urethane acrylates are available commercially from Bayer AG, Leverkusen, DE as Roskudyl® UA VP LS 2337, Roskudyl® UA VP LS 2396 or Roskudyl® UA XP 2510.

Additionally, the reactive diluents already described and known in the art of radiation-curing coatings may be used as a constituent of c), provided that they do not contain any NCO-reactive groups.

Compounds of component d) can be saturated or unsaturated. Chemical functionalities reacting with NCO groups are functionalities containing activated hydrogen atoms, such as hydroxyl, amine or thiol.

Preference is given to saturated polyhydroxy compounds, examples being the polyether polyols, polyester polyols, polycarbonate polyols, poly(meth)acrylate polyols and/or polyurethane polyols which are known from the technology of coating, adhesive bonding, printing inks and sealants and which contain no groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation.

Unsaturated hydroxy-functional compounds are, for example, the epoxy acrylates, polyester acrylates, polyether acrylates, urethane acrylates and acrylated polyacrylates which are known in the art of radiation-curing coatings and have an OH number of from 30 to 300 mg KOH/g.

It is additionally possible to use the reactive diluents, already described and known in the art of radiation-curing coatings, as a constituent of d), provided that they contain NCO-reactive groups.

As initiators of component e) for a free-radical polymerization it is possible to employ initiators which can be activated thermally and/or by radiation. Photoinitiators, which are activated by UV or visible light, are preferred in this context. Photoinitiators are compounds known per se, being sold commercially, a distinction being made between unimolecular (type I) and bimolecular (type II) initiators. Suitable (type I) systems are aromatic ketone compounds, e.g. benzophenones in combination with tertiary amines, alkylbenzophenones, 4,4'-bis(dimethylaminobenzophenone (Michler's ketone), anthrone and halogenated benzophenones or mixtures of the types stated. Of further suitability are (type II) initiators such as benzoin and its derivatives, benzil ketals, acylphosphine oxides, 2,4,6-trimethylbenzoylphosphine oxide for example, bisacylphosphine oxides, phenylglyoxylic esters, camphorquinone, α-aminoketophenones, α-α-di-alkoxyacetophenones and α-hydroxalkylphosphine oxides.

The initiators, which are used in amounts between 0.1% and 10% by weight, preferably 0.1% to 5% by weight, based on the weight of the film-forming binder, can be used as an individual substance or, on account of frequent advantageous synergistic effects, in combination with one another.

Where electron beams are used instead of UV irradiation there is no need for a photoinitiator. Electron beams, as is known to the skilled person, are generated by means of thermal emission and accelerated by way of a potential difference. The high-energy electrons then pass through a titanium foil and are guided onto the binders to be cured. The general principles of electron beam curing are described in detail in "Chemistry & Technology of UV & EB Formulations for Coatings, Inks & Paints", Vol. 1, P.K. T Oldring (Ed.), SITA Technology, London, England, pp. 101-157, 1991.

In the event of thermal curing of the activated double bonds, this can also take place with addition of thermally decomposing free-radical initiators. Suitability is possessed, as is known to the skilled person, by, for example, peroxy compounds such as dialkyl peroxides and peroxycarbonate, dialkyl peroxides such as, for example, diethyl peroxide, peresters of aromatic or aliphatic acids such as, for example, tert-butyl perbenzoate or tert-amyl peroxide 2-ethylhexanoate, inorganic peroxides such as, for example, ammonium peroxodisulfate, potassium peroxodisulfate, organic peroxides such as, for example, 2,2-bis(tert-butylperoxy)butane, dicumyl peroxide, tert-butyl hydroperoxide or else azo compounds such as 2,2'-azobis[N-(2-propenyl)-2-methylpropionamides], 1-[cyano-1-methylpropyl]formamides, 2,2'-azobis(N-butyl-2-methylpropionamides), 2,2'-azobis(N-cyclohexyl-2-methylpropionamides), 2,2'-azobis[2-methyl-
N-[2-[1-hydroxy-butyll][propionamides], 2,2'-azobis[2-
methyl-N-[2-[1-hydroxy-butyll][propionamides], 2,2'-
azobis[2-methyl-N-[1,1-bis(hydroxy-methyl)]-2-
hydroxyethyl]propionamides. Also possible are highly 
substituted 1,2-diphenylethenes (benzpinacols), such as, for 
example, 3,4-dimethyl-3,4-diphenylhexane, 1,1,2,2-tet-
raphenylenetane-1,2-diol or else the silylated derivatives 
thereof.

It is also possible to use a combination of initiators acti-
vable by UV light and thermally. The auxiliaries and additives 
of component e) include solvents of the type specified above 
under E).

Additionally it is possible for e), in order to increase the 
weather stability of the cured coating film, to comprise UV 
absorbers and/or HALS stabilizers as well. Preference is 
given to the combination. The former ought to have an 
absorption range of not more than 390 nm, such as triphenyl-
triazine types (e.g. Tinuvin® 400 (Ciba Spezialitätenchemie 
GmbH, Lampertheim, Del.), benzotriazoles such as Tinu-
vin® 622 (Ciba Spezialitätenchemie GmbH, Lampertheim, 
Del.) or oxadiazolines (e.g. Sandurvar® 3206 (Clariant, 
Muttenz, CH)) and are added at 0.5%–3.5% by weight, based 
on resin solids. Suitable HALS stabilizers are available com-
mercially (Tinuvin® 292 or Tinuvin® 123 (Ciba Spezialitä-
tenchemie GmbH, Lampertheim, Del.) or Sandurvar® 3258 
(Clariant, Muttenz, CH). Preferred amounts are 0.5%–2.5% 
by weight, based on resin solids.

It is likewise possible for e) to comprise pigments, dyes, 
fillers, levelling additives and devolatilizing additives.

Additionally it is possible, if necessary, for the catalysts 
known from polyurethane chemistry for accelerating the 
NCO/OH reaction to be present in e). These are, for example, 
tin salts or zinc salts or organomino compounds, tin soaps and/or 
zinc soaps such as, for example, tin octoate, dibutyltin dilau-
rate, dibutyltin oxide or tertiary amines such as diazacyclo-
[2.2.2]octane (DACBO).

The application of the coating compositions of the inven-
tion to the material to be coated takes place with the methods 
known and customary in coatings technology, such as spray-
ing, knife coating, rolling, pouring, dipping, spin coating, 
brushing or squirting or by means of printing techniques such 
as screen, gravure, flexographic or offset printing and also by 
means of transfer methods.

Suitable substrates are, for example, wood, metal, includ-
ing in particular metal as used in the applications of wire 
enameiling, coil coating, can coating or container coating, and 
also plastic, including plastic in the form of films, especially 
ABS, AMMA, ASA, CA, CAB, EP, UP, CF, ME, MDF, MF, PE, 
PA, PE, HDPE, LDPE, LLDPE, UHMWPE, PET, PMMA, PP, PS, 
SH, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, 
BMI, PP-EPDM, and UP (abbreviations according to DIN 772811), 
paper, leather, textiles, felt, glass, wood, wood materials, cork, inorganically bonded substrates such as wooden boards and fibre cement slabs, electronic 
assemblies or mineral substrates. It is also possible to coat 
substrates consisting of a variety of the abovementioned 
materials, or to coat already coated substrates such as 
vehicles, aircraft or boats and also parts thereof, especially 
vehicle bodies or parts for exterior mounting. It is also pos-
ible to apply the coating compositions to a substrate tempo-
rary, then to cure them partly or fully and optionally to 
detach them again, in order to produce films, for example.

For curing it is possible for solvents present, for example, 
to be removed entirely or partly by flushing off.

Subsequently or simultaneously it is possible for the 
optionally necessary thermal and the photochemical curing 
operation or operations to be carried out in succession or 
simultaneously. If necessary the thermal curing can take place 
at room temperature or else at elevated temperature, prefer-
ably at 40–106°C, preferably at 60–130°C, more preferably at 
80–110°C.

Where photoinitiators are used in e) the radiation cure takes 
place preferably by exposure to high-energy radiation, in 
other words UV radiation or daylight, such as light of wave-
length 200 to 700 nm or by bombardment with high-energy 
electrons (electron beams, 150 to 300 keV). Radiation 
sources of light or UV light used are, for example, high-
pressure or medium-pressure mercury vapour lamps, it being 
possible for the mercury vapour to have been modified by 
doping with other elements such as gallium or iron. Lasers, 
pulsed lamps (known under the designation of UV flashligh-
t lamps), halogen lamps or excimer emitters are likewise pos-
sible. As an inherent part of their design or through the use 
of special filters and/or reflectors, the emitters may be equipped 
so that part of the UV spectrum is prevented from being 
emitted. By way of example, for reasons of occupational 
hygiene, for example, the radiation assigned to UV-C or to 
UV-C and UV-B may be filtered out. The emitters may be 
installed in stationary fashion, so that the material for irra-
diation is conveyed past the radiation source by means of a 
mechanical device, or the emitters may be mobile and the 
material for irradiation may remain stationary in the course of 
curing. The radiation dose which is normally sufficient for 
crosslinking in the case of UV curing is situated in the range 
from 80 to 5000 mJ/cm².

Irradiation can if desired also be carried out in the absence 
of oxygen, such as under an inert gas atmosphere or an oxy-
gen-reduced atmosphere. Suitable inert gases are preferably 
nitrogen, carbon dioxide, noble gases or combustion gases.

Irradiation may additionally take place by covering the coat-
ing with media transparent to the radiation. Examples of such 
are, for example, polymeric films, glass or liquids such as 
water.

Depending on the radiation dose and curing conditions it is 
possible to vary the type and concentration of any initiator 
used, in a manner known to the skilled person.

Particular preference is given to carrying out curing using 
high-pressure mercury lamps in stationary installations. Pho-
toinitiators are then employed at concentrations of from 0.1% 
10 to 10% by weight, more preferably from 0.2% to 3.0% by 
weight, based on the solids of the coating. For curing these 
coatings it is preferred to use a dose of from 200 to 3000 
mJ/cm², measured in the wavelength range from 200 to 600 
nm.

In the case of use of thermally activable initiators in d) 
by increasing the temperature. The thermal energy may be intro-
duced into the coating by means of radiation, thermal con-
duction and/or convection, it being customary to employ the 
ovens, near-infrared lamps and/or infrared lamps that are 
conventional in coatings technology.

The applied film thicknesses (prior to curing) are typically 
below 0.5 and 5000 μm, preferably below 5 and 1000 μm, 
more preferably between 15 and 200 μm. Where solvents are 
used, it is removed after application and before curing, by 
the customary methods.

EXAMPLES

All percentages are by weight unless indicated otherwise.

The determination of the NCO contents in % was under-
taken by back-titration with 0.1 mol/l hydrochloric acid fol-
lowing reaction with butylamine, on the basis of DIN EN ISO 11909.
The viscosity measurements were carried out with a cone-plate viscometer (SM-KP), Viskolab LC3/ISO from Paar Physica, Ostfildern, DE in accordance with ISO/DIS 3219: 1990.

Infrared spectroscopy was on liquid films applied between sodium chloride plates on a model 157 instrument from Perkin Elmer, Überlingen, DE.

The amounts of trimers, uretdione, allophanate and urethane structures in the end product were determined by means of NMR spectroscopy. For this purpose, $^{1}H$-NMR spectra of a sample were recorded in CDCl$_3$, (DPX 400 and AVC 400 from Bruker, Karlsruhe, DE; resonance frequency 100 MHz, relaxation delay 4 s, 2000 scans, acquisition time 1.03 seconds and angle of excitation $30^\circ$ C.) and the molar proportions of the substructures were determined from the signal integrations at $\delta$($^1H$)=121.4 ppm (1C, NCO), 148.4 ppm (3C, trimers), 153.8 ppm (1C, allophanate), 156.3 ppm (1C, urethane) and 157.1 ppm (2C, uretdione).

The amount of residue monomers and amount of volatile synthesis components were analyzed by means of GC (method using tetradecane as internal standard, oven temperature $110^\circ$ C., injector temperature $150^\circ$ C., carrier gas helium, instrument: 6890 N, Agilent, Waldbronn, DE; column: Restek RT 50, 30 m, 32 mm internal diameter, film thickness 0.25 mm).

The solids was determined in accordance with DIN 53216/1 draft 4/89, ISO 3251.

The ambient temperature of 23$^\circ$ C. prevailing at the time when the experiments were conducted is referred to as RT.

Desmonopip® N 3400: HDI polyisocyanate predominantly containing uretdione structure, viscosity 185 mPas/$23^\circ$ C, NCO content 21.4%, commercial product of Bayer AG, Leverkusen, DE.

Desmonopip® Z: dibutyltin dilaurate (DBTL), commercial product of Bayer AG, Leverkusen, DE.

Darocur® 1173 photoinitiator, commercial product of Ciba Spezialitätenchemie GmbH, Lampertheim, DE.

Tone® M100: reaction product of 2 equivalents of e-caprolactone with 1 equivalent of 2-hydroxyethyl acrylate, OH content 4.97%, viscosity 82 mPas/$23^\circ$ C, commercial product of Dow, Schwalbach, DE.

Examples 1-5 describe the preparation of catalytically active phenoxides, which in Examples 4-5 are used for the reaction of compounds containing uretdione groups with ethylenically unsaturated hydroxy compounds to form corresponding compounds containing allophanates.

Example 1

Tetraethylammonium 4-(Methoxycarbonyl)Phenoxyde

A glass flask with reflux condenser, heatable oil bath, mechanical stirrer and internal thermometer was charged at room temperature with 38.00 g of methyl 4-hydroxybenzoate and 277.92 g of water and these components were stirred together thoroughly. Subsequently 162.00 g of tetrabutylammonium hydroxide (40% strength in water) were added and the reaction mixture was heated to 60$^\circ$ C. It was stirred at 60$^\circ$ C. for one hour (the contents of the flask become clear). Then the reaction mixture was cooled and the water was distilled off under reduced pressure, 20 mbar, at 30-45$^\circ$ C. The product was then washed with butyl acetate and dried at 80$^\circ$ C. and 10 mbar in a vacuum drying cabinet. This gave a white solid.
was charged at RT with 53.48 g of Desmodur® N3400, 0.08 g of 2,6-di-tert-butyl-4-methylphenol and 0.001 g of Desmorapid® Z and this initial charge was then heated to 60°C. 31.83 g of 2-hydroxyethyl acrylate were slowly added dropwise, in the course of which a maximum temperature of 70°C was attained. Thereafter the reaction mixture was held at 70°C until the NCO content <0.1%. Subsequently a mixture of 15.66 g of 2-hydroxyethyl acrylate and 0.51 g of the catalyst from Example 3 was added dropwise. The reaction mixture was heated to and held at 80°C until in the IR spectrum at ν=1768 cm⁻¹ after 3.5 h only a very weak signal for uretdione groups was detectable. 0.10 g of benzyl chloride was added and the mixture was cooled rapidly to RT. A sample taken was found by gas chromatography to have a hydroxyethyl acrylate content of 4.15%. 6.8 g of hydroxyethyl acrylate were added and the mixture was stirred at 80°C until in the IR spectrum at ν=2272 cm⁻¹ there was no longer any signal for the isocyanate group. The hydroxyethyl acrylate content of a sample taken was found by gas chromatography to be 0.07%. The product obtained was clear and had a viscosity of 56,500 mPa·s/25°C and an NCO content of 0%.

Comparative Example C1

Attempt to Prepare an Allophanate-Containing Binder

The catalysts described in US-A 2003 301 537 13 for the crosslinking of powder coating materials comprising uretdione-group-containing curing agents and polymeric hydroxyl compounds without activated double bonds were examined for suitability:

Example 5 was repeated with the difference that, instead of the catalyst from Example 3, now 0.51 g of tetrabutylammonium hydroxide was used as catalyst. The reaction mixture was heated to and held at 80°C until in the IR spectrum at ν=1768 cm⁻¹ after 2 h only a very weak signal for uretdione groups was detectable. 0.10 g of benzyl chloride was added and the mixture was cooled rapidly to RT. In the course of this cooling the reaction mixture turned cloudy. The hydroxyethyl acrylate content of a sample taken was found by gas chromatography to be 2.4%. 5.20 g of Desmodur® N3400 were added to the reaction mixture, which was stirred at 70°C until in the IR spectrum at ν=2272 cm⁻¹ there was no longer any signal for the isocyanate group. The hydroxyethyl acrylate content of a sample taken was found by gas chromatography to be 0.17%. A cloudy product was obtained with a viscosity of 84,000 mPa·s/25°C and an NCO content of 0%.

Comparative Example C2

Attempt to Prepare an Allophanate-Containing Binder

The catalysts described in US-A 2003 301 537 13 for the crosslinking of powder coating materials comprising uretdione-group-containing curing agents and polymeric hydroxyl compounds without activated double bonds were examined for suitability:

Example 5 was repeated with the difference that, instead of the catalyst from Example 3, now 0.67 g of tetrabutylammonium fluoride was used as catalyst. The reaction mixture was heated to and held at 80°C until in the IR spectrum at ν=1768 cm⁻¹ after 3 h only a very weak signal for uretdione groups was detectable. 0.10 g of benzyl chloride was added and the mixture was cooled rapidly to RT. In the course of this cooling the reaction mixture turned cloudy, and a colourless precipitate formed. The hydroxyethyl acrylate content of a sample taken was found by gas chromatography to be 1.7%. 4.30 g of Desmodur® N3400 were added to the reaction mixture, which was stirred at 70°C until in the IR spectrum at ν=2272 cm⁻¹ there was no longer any signal for the isocyanate group. The hydroxyethyl acrylate content of a sample taken was found by gas chromatography to be 0.15%. A cloudy product was obtained with a viscosity of 92,000 mPa·s/25°C and an NCO content of 0%.

Comparative Examples 6 and 7 show that the substances which are suitable for crosslinking powder coating materials composed of uretdione-group-containing curing agents and polymeric hydroxyl compounds are not suitable for the targeted synthesis of allophanates from uretdiones and alcohols. The products thus obtained are clouded and of relatively high viscosity, so making them unsuitable for producing coatings.

Example 6

Coating Formulation and Coating Material

A portion of the product from Example 5 was mixed thoroughly with 3.0% of the photoinitiator Durcor® 1173. Using a bone doctor blade with a gap of 90 μm the mixture was drawn down in the form of a thin film onto a glass plate. UV irradiation (medium pressure mercury lamp, IST Metz GmbH, Nürtingen, DE, 750 mJ/cm²) gave a hard, transparent coating which could not be damaged by scratching using steel wool (grade 0/0/0) in ten back-and-forth strokes with a force of 500 g directed onto the film.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

What is claimed is:

1. Binders containing allophanate groups and containing groups capable of participating in a polymerization reaction with ethynlically unsaturated compounds on exposure to actinic radiation, obtained by a process comprising:
   1) reacting via urethanization:
      A) the NCO groups of one or more compounds containing uretdione groups and NCO groups with
      B) the OH groups of one or more OH-functional compounds containing ethynlically unsaturated groups polymerizable on exposure to actinic radiation, and
   2) reacting via allophanatization:
      the reaction product of step 1) with one or more compounds B) and
      C) optionally further NCO-reactive compounds, the reaction via allophanatization occurring in the presence of D) one or more compounds containing phenoxide groups, as catalysts.

2. Binders containing allophanate groups according to claim 1, wherein the binders have a viscosity at 23°C of ≥100,000 mPa·s.

3. A method of preparing coatings, coating materials, adhesives, printing inks, casting resins, dental compounds, sizes, photosists, stereolithography systems, resins for composite materials and sealants comprising combining the binders containing allophanate groups according to claim 1 and one or more additives selected from the group consisting of UV absorbers, HALS stabilizers, pigments, dyes, fillers, levelling additives, devolatilizing additives, catalysts, and combinations thereof.
Coating compositions comprising

a) one or more binders containing allophanate groups, according to claim 1,

b) optionally one or more polyisocyanates containing free or blocked isocyanate groups, which are free from groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation,

c) optionally other compounds, different from those of a), which contain groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally contain free or blocked NCO groups,

d) optionally one or more isocyanate-reactive compounds containing active hydrogen,

e) initiators,

f) optionally solvents and
g) optionally auxiliaries and additives.

Substrates coated with coatings obtained from binders containing allophanate groups, according to claim 1.

Coating compositions comprising

a) one or more binders containing allophanate groups, according to claim 5.

b) optionally one or more polyisocyanates containing free or blocked isocyanate groups, which are free from groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation,

c) optionally other compounds, different from those of a), which contain groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally contain free or blocked NCO groups,

d) optionally one or more isocyanate-reactive compounds containing active hydrogen,

e) initiators,

f) optionally solvents and
g) optionally auxiliaries and additives.

Substrates coated with coatings obtained from binders containing allophanate groups, according to claim 6.

Binders containing allophanate groups and containing groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation, obtained by a process comprising:

1) reacting via urethanization:
A) the NCO groups of one or more compounds containing uretdione groups and NCO groups, said compounds being based on hexamethylene disiocyanate, with
B) the OH groups of one or more OH-functional compounds containing ethylenically unsaturated groups polymerizable on exposure to actinic radiation, and

2) reacting via alkoxyanation:
the reaction product of step 1) with
one or more compounds B) and

C) optionally further NCO-reactive compounds, the reaction via alkoxyanation occurring in the presence of D) one or more compounds containing phenoxy groups, as catalysts.

Binders containing allophanate groups according to claim 8, wherein the binders have a viscosity at 23°C of $\geq 100,000$ mPas.

A method of preparing coatings, coating materials, adhesives, printing inks, casting resins, dental compounds, sizes, photoresists, stereolithography systems, resins for composite materials and sealants comprising combining the binders containing allophanate groups according to claim 9 and one or more additives selected from the group consisting of UV absorbers, HALS stabilizers, pigments, dyes, fillers, levelling additives, devolatilizing additives, catalysts, and combinations thereof.

Coating compositions comprising

a) one or more binders containing allophanate groups, according to claim 9.

b) optionally one or more polyisocyanates containing free or blocked isocyanate groups, which are free from groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation,

c) optionally other compounds, different from those of a), which contain groups capable of participating in a polymerization reaction with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally contain free or blocked NCO groups,

d) optionally one or more isocyanate-reactive compounds containing active hydrogen,

e) initiators,

f) optionally solvents and
g) optionally auxiliaries and additives.

Substrates coated with coatings obtained from binders containing allophanate groups, according to claim 11.

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